

Optical study of the metal-nonmetal transition in $\text{Ni}_{1-\delta}\text{S}$

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Optical reflectivity study has been made on the hexagonal (NiAs-type) $\text{Ni}_{1-\delta}\text{S}$ in order to probe its electronic properties, in particular those associated with the metal-nonmetal transition in this compound. Samples with $\delta=0.005$ and 0.02 are studied, which have transition temperatures $T_t=246$ K and 161 K, respectively. A pronounced dip appears in the reflectivity spectra upon the transition, and the optical conductivity spectra show that the electronic structure below T_t is similar to that of a carrier-doped semiconductor with an energy gap of ~ 0.15 eV. The optical spectra indicate that the gap becomes larger with decreasing temperature, and it becomes smaller as δ increases. It is also found that the overall spectrum including the violet region can be described based on a charge-transfer-type semiconductor, consistent with recent photoemission results.

Keywords: D. optical properties, D. phase transitions

The problem of the metal-nonmetal phase transition in the hexagonal NiS has been studied for three decades, but the transition mechanism is not completely understood yet. The high temperature (HT) phase above the transition temperature, $T_t \sim 260$ K, is a paramagnetic metal. Upon cooling through T_t , the resistivity increases suddenly by a factor of ~ 40 , associated with slight increase in the lattice constants (0.3 % in a and 1 % in c) and the appearance of an antiferromagnetic order.¹⁻³ T_t is lowered sharply with increasing Ni vacancies, and the transition disappears when the vacancy content exceeds ~ 4 %.⁴ Similar behavior is observed also with an applied pressure, and the transition is not observed at pressures above ~ 2 GPa.⁵ These behaviors are summarized in the phase diagram of Fig. 1.

The nature of the low-temperature (LT) phase below T_t has been studied by many experiments. The resistivity (ρ) increases only slightly with cooling, with an activation energy of several meV.⁴ In contrast, an optical study by Barker and Remeika⁶ clearly showed the presence of an energy gap of about 0.15 eV. Hall effect experiment by Ohtani⁴ has shown that the majority carrier in the LT phase is the hole, and the density of holes is proportional to that of Ni vacancies, with ~ 2 holes per Ni vacancy. Namely, the LT phase can be described as a p -type degenerate semiconductor, where the Ni vacancies act as acceptors. Effects of substituting other elements for Ni or S have been also studied in detail.^{7,8} Recently, two high-resolution photoemission studies^{9,10} have revealed a finite density of states (DOS) around the Fermi energy (E_F) in the LT phase, but they have given contrasting interpretations: Nakamura *et al.*⁹ have concluded that

there is a small correlation-induced band gap with an unusually sharp band edge, and that the observed finite DOS at E_F is due to thermal and instrumental broadenings of the edge. On the other hand, Sarma *et al.*¹⁰ have concluded that the LT phase is an “anomalous metal”.

Various models have been proposed to account for the phase transition and the gap opening in NiS. At early stage, it was proposed that the transition was a Mott-type transition.¹¹ Namely, the Ni $3d$ band splits into two bands separated by a gap in the LT phase due to strong Coulomb interaction at Ni sites. It was also proposed that the semiconducting electronic structure was caused by the antiferromagnetic order.¹² Band calculations that take into account many-body effects via various approximations have been unable to reproduce an energy gap with a reasonable magnitude.⁹ More recently, it has been proposed, based on cluster-model calculations and photoemission experiments, that the energy gap in NiS is of charge-transfer type, namely the energy gap in NiS is formed between the upper $3d$ and the S $3p$ bands.¹³⁻¹⁵

Here we report our optical reflectivity study on the electronic structure of $\text{Ni}_{1-\delta}\text{S}$. We observe large spectral changes upon the phase transition, showing the formation of an energy gap of ~ 0.15 eV in agreement with the earlier optical work.⁶ Our present work, however, reveals more detailed temperature-dependence of the spectra, and provides a comparison between samples having different T_t . The optical gap in the LT phase becomes larger with decreasing temperature, and also the gap becomes smaller as δ increases. In addition, we show that the overall spectra including the violet region can be understood assuming a charge-transfer semiconductor, con-

sistent with the cluster-model calculations and photoemission experiments.^{13–15}

The samples used in this work were polycrystalline $\text{Ni}_{1-\delta}\text{S}$ prepared as follows. Ni and S powders were mixed with mole ratios of $[\text{Ni}]:[\text{S}]=1:1$ and $0.98:1$, and melted at 1000 C° in an evacuated quartz tube. Then they were annealed at 700 C° for 2 days and at 500 C° for 1 week, and quenched in iced water. The $1:1$ mixture resulted in an ingot with $T_t=246\text{ K}$, and the $0.98:1$ mixture with $T_t=161\text{ K}$. Comparing these T_t values with a previously-reported $T_t - \delta$ diagram,⁷ the vacancy contents in these samples are estimated to be $\delta \sim 0.005$ (or $\text{Ni}_{0.995}\text{S}$, $T_t = 246\text{ K}$) and $\delta \sim 0.02$ ($\text{Ni}_{0.98}\text{S}$, $T_t = 161\text{ K}$).¹⁶ The ingots were cut into disk-shaped samples, and the surface was mechanically polished with alumina powders. Then the samples were annealed at 500 C° for 3 days in an evacuated quartz tube, followed by a quench in iced water. This re-annealing process is necessary because the mechanical cutting and polishing suppress the phase transition in the sample surface.⁶ Reflectivity measurements below 2.5 eV were done using a rapid-scan Fourier interferometer (Bruker Inc. IFS-66v) and conventional sources. Measurements between 2 eV and 30 eV were done using synchrotron radiation source at the beamline BL7B of the UVSOR Facility, Institute for Molecular Science. Standard near-normal incidence configuration was used for the reflectivity measurements. An optical conductivity spectrum $\sigma(\omega)$ was obtained from a measured reflectivity spectrum $R(\omega)$ using the Kramers-Kronig relations.¹⁷ Hagen-Rubens ($1 - a\sqrt{\omega}$) and ω^{-4} extrapolation functions were used to complete the lower- and higher-energy ends of the reflectivity spectra.

Figure 2 shows the infrared $R(\omega)$ of $\text{Ni}_{0.995}\text{S}$ and $\text{Ni}_{0.98}\text{S}$ measured at several temperatures. The inset shows the $R(\omega)$ of $\text{Ni}_{0.995}\text{S}$ at room temperature up to 30 eV . For both samples, the most significant spectral change upon the transition is a large reduction of $R(\omega)$ in the infrared region, accompanied by a “dip” near 0.15 eV . The result for $\text{Ni}_{0.995}\text{S}$ is very similar to the single crystal result of Barker and Remeika⁶. These spectral changes occurred over a temperature width of a few K around T_t , as observed on our rapid-scan spectrometer while cooling down slowly. With cooling further in the LT phase, the dip blue-shifts slightly, which is seen clearer for $\text{Ni}_{0.995}\text{S}$. Figure 3 shows the corresponding $\sigma(\omega)$ spectra. For both samples, $\sigma(\omega)$ has a sharp rise toward lower energy in the HT phase, which is typical of a good metal. Below T_t , however, the spectral weight below $\sim 0.3\text{ eV}$ is strongly depleted with an “onset” of $\sigma(\omega)$ at $\sim 0.15\text{ eV}$, which is indicated by the arrows in Fig. 3. Below the onset, there exists a small rise in $\sigma(\omega)$. This metallic, Drude-like spectral component indicates that there are a small but sizable amount of free carriers in the LT phase. These optical spectra suggest that the LT phase is a semiconductor with an energy gap of $\sim 0.15\text{ eV}$ and excess carriers, or equivalently a carrier-doped semiconductor. This is consistent with the Hall effect result,⁴ which showed that there were rather high density of holes ($\sim 10^{21}\text{ cm}^{-3}$)

in the LT phase. Another possible interpretation for the LT phase from these optical spectra is a semimetal, that has a low carrier concentration and a strong reduction in the DOS around E_F , or a “psedogap”. It is seen that the blue-shift of the dip in $R(\omega)$ with cooling has a corresponding blue-shift of the onset in $\sigma(\omega)$, which shows that the energy gap becomes larger with decreasing temperature. This behavior of NiS was previously unknown. Note that a measurement of $\rho(T)$ would not give this information, since for a p -type semiconductor the activation energy given by $\rho(T)$ is connected to acceptor-related states at low temperatures,¹⁸ rather than that associated with the intrinsic energy gap.

Although the spectral changes upon the phase transition are qualitatively similar for the two samples, there are important differences: (i) The Drude-like component in the LT phase has much larger spectral weight for $\text{Ni}_{0.98}\text{S}$ than for $\text{Ni}_{0.995}\text{S}$. (ii) The onset in $\sigma(\omega)$ is lower in energy for $\text{Ni}_{0.98}\text{S}$ than for $\text{Ni}_{0.995}\text{S}$. (i) indicates that there are much more free carriers in the LT phase of $\text{Ni}_{0.98}\text{S}$ than that of $\text{Ni}_{0.995}\text{S}$. This is consistent, since $\text{Ni}_{0.98}\text{S}$ contains more holes than $\text{Ni}_{0.995}\text{S}$ due to larger density of Ni vacancies.⁴ (ii) indicates that $\text{Ni}_{0.98}\text{S}$ has a smaller energy gap than NiS. This observation implies that the energy gap in the LT phase becomes smaller as δ (Ni vacancy content) increases. This is another important result in this work. The reason for this gap narrowing with increasing δ is unclear at present. The lattice constants become smaller as δ increases,⁷ which may broaden the bands above and below the gap, resulting in a narrower gap. On the other hand, increasing δ also leads to a larger carrier density and a larger acceptor-related DOS around E_F . It is likely that the observed gap narrowing and the lowering of T_t with increasing δ result from a complicated interplay among these effects.

Recently, Sarma *et al.*¹⁰ have reported a high-resolution photoemission study of NiS. They observed a metallic electronic structure in the LT phase, where the DOS at E_F was nearly flat and smoothly varying, and was also slightly smaller than that in the HT phase. Contrasting the metallic electronic structure around E_F to the weakly temperature-dependent ρ and the large optical gap, they argued that the LT phase was an “anomalous metal”. However, a metallic DOS *within the close vicinity of E_F* is not necessarily inconsistent with a small variation in $\rho(T)$ and a large gap in the LT phase, since these behaviors can be viewed as typical of a p -type, degenerate semiconductor.^{4,18} Namely, in a degenerate p -type semiconductor, E_F is located near the top of the valence band, where a large acceptor-related DOS is present. Then it is possible to have a metallic (continuous) DOS around E_F which is smaller than that for the HT phase (good metal). For such case, the activation energy measured by $\rho(T)$ at low temperatures probes the activation of holes to these low-lying states near E_F , and it is not directly related to the intrinsic gap. It has been demonstrated convincingly that the LT phase of NiS is a p -type, degenerate semiconductor by Ohtani⁴, and the present optical

result gives further support to this picture.

Although we have described the LT phase as a carrier-doped semiconductor, it does not mean at all that the LT phase is a “conventional” semiconductor. The holes in the LT phase are probably under the influence of strong on-site Coulomb interaction, and it is likely that the holes do not show simple free-particle behaviors. In this respect, the behaviors of the holes in the LT phase are very interesting and deserve further studies.

Fujimori *et al.*^{13–15} have performed cluster-model calculations for NiS that take into account many-body and inter-configuration interactions. Comparing the calculated results with the measured photoemission (PE) spectra, they have concluded that the energy gap in NiS is a charge-transfer (CT) gap that opens between Ni 3*d*- and S 3*p*-derived bands, rather than a Mott-Hubbard gap between the correlation-split 3*d* bands. Figure 4 illustrates optical transitions in these two cases. The gap excitation is a *p*-*d* transition in the CT case, while it is a *d*-*d* transition in the Mott-Hubbard case. Note that a *d*-*d* transition is optically forbidden, but vacancy-related disorder and *p*-*d* hybridization may make the transition partially allowed. Regarding the infrared gap of NiS as a CT gap, the broad absorption band in $\sigma(\omega)$ at $0.2 \text{ eV} \leq \hbar\omega \leq 2.5 \text{ eV}$ (Fig. 3) can be attributed to optical transitions from the S 3*p* band¹⁹ to the upper Ni 3*d* band, or equivalently to charge transfers from S to Ni. Then, the weak peak near 4.5 eV in $\sigma(\omega)$, seen in the inset of Fig. 1, can be assigned to transitions from the lower 3*d* to the upper 3*d* bands (indicated by the dashed arrow in Fig. 4). The observed peak energy is in good agreement with the estimated on-site Coulomb interaction energy, $U = 4.0 \pm 0.5 \text{ eV}$, given by Fujimori *et al.*¹⁴

In conclusion, we have presented an optical reflectivity study of $\text{Ni}_{1-\delta}\text{S}$. The optical spectra in the infrared show large changes upon the phase transition, and the spectra for the LT phase can be described as a carrier-doped semiconductor with an energy gap of $\sim 0.15 \text{ eV}$. The magnitude of the optical gap became larger with decreasing temperature, and it became smaller for larger δ . The overall spectrum including the violet region can be understood based on a charge-transfer-type semiconductor, consistent with previous photoemission results and cluster-model calculations. Further work is in progress in wider ranges of δ ($0.005 \leq \delta \leq 0.04$), temperatures ($8 \text{ K} \leq 295 \text{ K}$), and photon energies (down to far-infrared), and quantitative analyses based on the sum rule for $\sigma(\omega)$ will provide further information on the metal-nonmetal transition of NiS.

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- ¹⁶ It is possible that even carefully prepared sintered NiS with $T_i \simeq 264 \text{ K}$ has a sizable amount of Ni vacancies, $\delta \leq 0.002$. [See Sawa, T. & Anzai, S. *J. Appl. Phys.* **49**, 1978, 5612.]
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- ¹⁹ Note that the “3*p* band” here is not purely derived from S, but there should be a strong hybridization with the Ni 3*d* band, since the gap is much smaller than the width of the absorption band.

FIG. 1. Schematic phase diagram of $\text{Ni}_{1-\delta}\text{S}$ in terms of temperature (T), Ni vacancy concentration (δ), and external pressure (P).

FIG. 2. (a) Infrared reflectivity (R) spectra of $\text{Ni}_{0.995}\text{S}$ and $\text{Ni}_{0.98}\text{S}$ measured at several temperatures. The inset shows R of $\text{Ni}_{0.995}\text{S}$ at 295 K up to 30 eV.

FIG. 3. Optical conductivity (σ) spectra of $\text{Ni}_{0.995}\text{S}$ and $\text{Ni}_{0.98}\text{S}$ below 2.5 eV at several temperatures. The arrows indicate the “onset” discussed in the text. The inset shows σ of $\text{Ni}_{0.995}\text{S}$ at 295 K up to 30 eV.

FIG. 4. Illustration of optical excitations across the energy gap for a charge-transfer insulator (a) and a Mott insulator (b). In (a), the gap is formed between the Ni $3d$ upper Hubbard band (UHB) and the S $3p$ band, while in (b) it is formed between UHB and the lower Hubbard band (LHB).

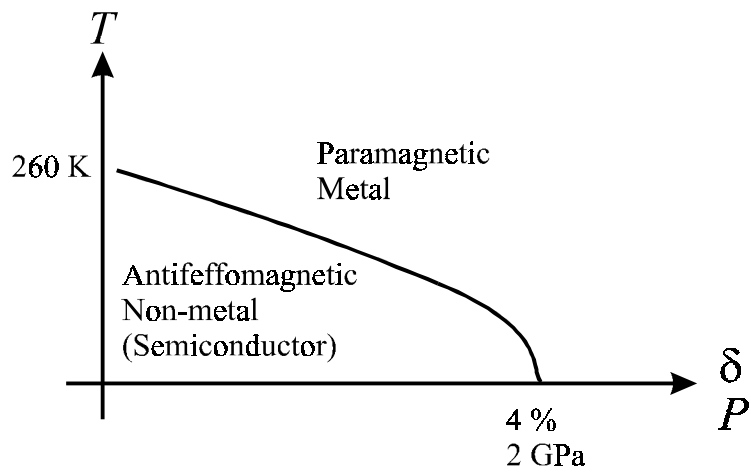


FIG. 1
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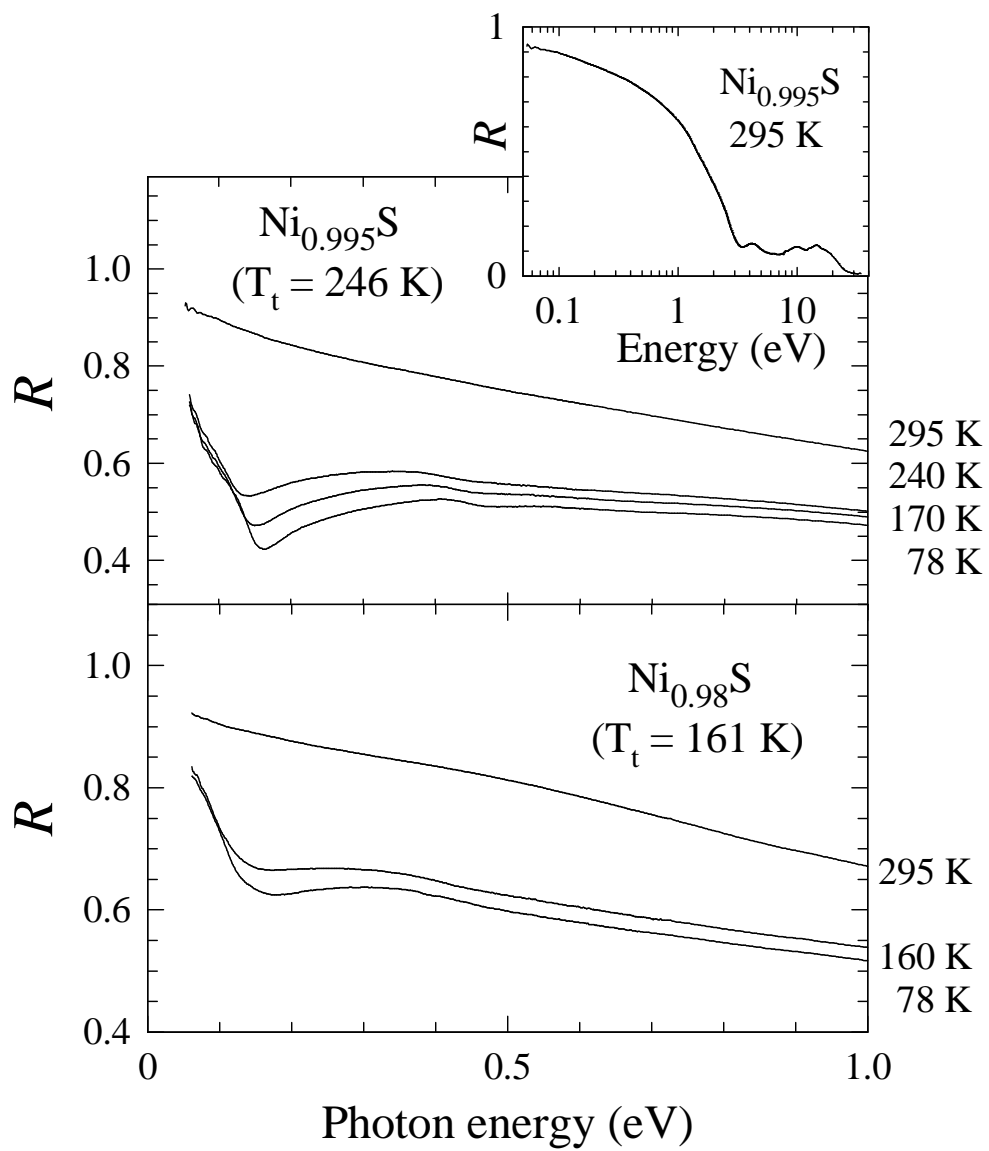


Fig.2
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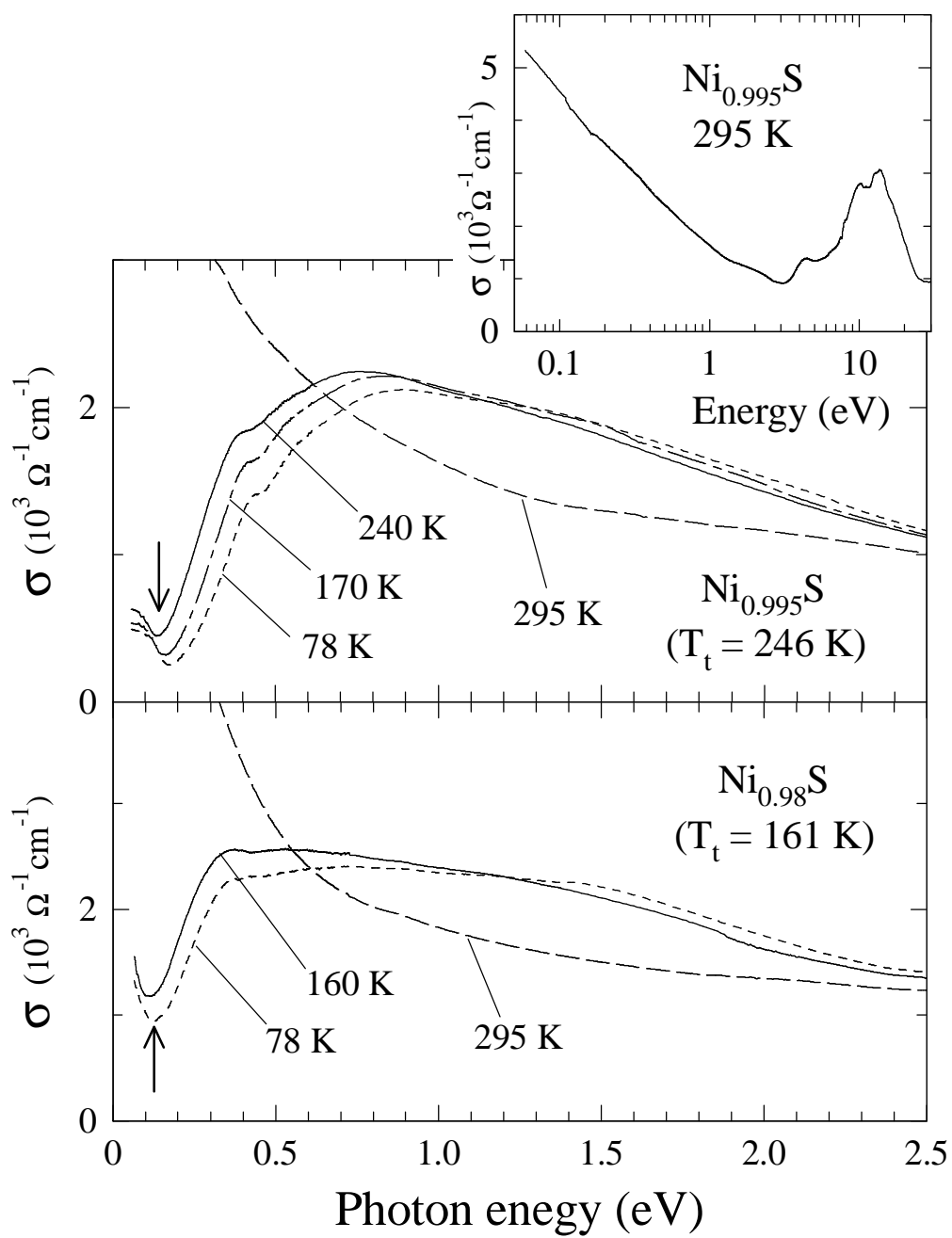


FIG.3
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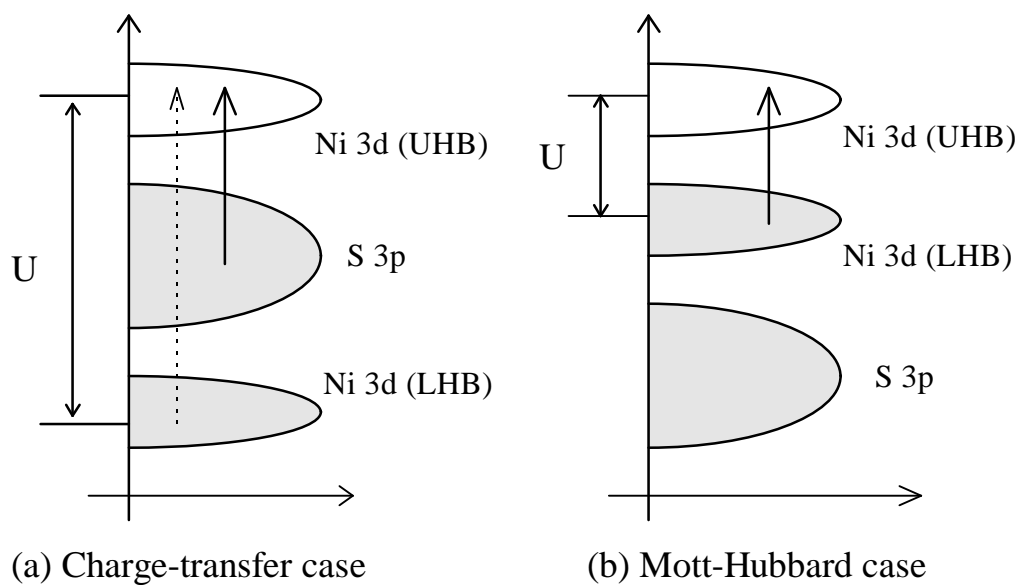


FIG. 4
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